Editor's choice

Density functional theory calculations of the non-resonant and resonant X-ray emission spectroscopy of carbon fullerenes and nanotubes

Magnus W.D. Hanson-Heine [a], Michael W. George [a,b], Nicholas A. Besley [a,*]

[a] School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK
[b] Department of Chemical and Environmental Engineering, University of Nottingham Ningbo China, 199 Taiking East Rd., Ningbo 315100, Zhejiang, China

ABSTRACT

The non-resonant X-ray emission spectroscopy of fullerenes and carbon nanotubes is studied with density functional theory in conjunction with short-range corrected functionals. For C_{60} and C_{70} the X-ray emission spectra are insensitive to modest structural changes, and absorption onto the fullerene cage has the greatest effect with a broader less structured band observed with the high energy π band reduced in intensity. For carbon nanotubes the X-ray emission spectra are shown to be weakly dependent on the length and chirality of the nanotube. However, some variation with the diameter of the tube is observed in both resonant and non-resonant spectra.

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1. Introduction

The increasing availability of synchrotron sources and free-electron lasers has led to spectroscopic techniques in the X-ray region being applied in a wide range of research areas [1–4]. One advantage of these techniques compared with other spectroscopic methods is that they are element specific and can provide a local probe of structure. More recently, these techniques have been used to study ultrafast chemical processes through time-resolved measurements [5–7]. There are several commonly used spectroscopic techniques in the X-ray region which can provide complementary information. For example, X-ray emission spectroscopy (XES) probes the occupied orbitals while X-ray absorption spectroscopy (XAS) probes the unoccupied orbitals. Resonant inelastic X-ray scattering (RIXS) represents an extension of XES wherein the intermediate state is a core-excited state rather than the core-ionised state in XES. Simulations of X-ray spectroscopy can play an important role in interpreting and understanding spectra measured by experiment. Within the framework of density functional theory (DFT), X-ray absorption spectra are commonly simulated using either transition-potential or time-dependent density functional theory (TDDFT) approaches [8,9]. Accurate core-excitation energies can be obtained from TDDFT calculations with the use of short-range corrected (SRC) functionals [10] and it has been shown how these calculations can be applied to study large systems [11].

There has been less focus on the calculation of XES, one approach is to apply TDDFT or equations of motion coupled cluster theory to a reference determinant describing the core-ionised state [12], and these approaches have been applied to study the XES of organic [13] and inorganic [14,15] molecules. Alternatively, X-ray emission spectra can be determined directly from a Kohn–Sham DFT calculation. In this approach the transition energy is evaluated from the orbital energies of the valence orbital (ϵ_v) and core orbital (ϵ_c)

$$\Delta E = \epsilon_v - \epsilon_c. \tag{1}$$

The associated intensity can be determined from the following transition matrix element

$$f \propto |\langle \phi_c | \hat{\mu} | \phi_v \rangle|^2 \tag{2}$$

where a valence orbital (ϕ_v) is taken to be the initial state and the final state is a core orbital (ϕ_c). Recently, it has been shown that this approach can provide accurate X-ray emission spectra when the DFT calculation is performed with a SRC exchange-correlation functional [16]. These functionals were introduced for the calculation of X-ray absorption spectra and incorporate an increased fraction of Hartree-Fock exchange in the short range (low r_{12}) in the evaluation of the exchange energy contribution. It was demonstrated that this approach could be extended to simulate RIXS in a two-step procedure where a reference determinant describing the intermediate core-excited state is used in the Kohn-Sham DFT calculation. Although it was necessary to average over a number of structures from a molecular dynamics (MD) simulation in the core-excited state to achieve a reasonable agreement with experiment. The importance of including vibrations via molecular dynamics

sampling has also been observed in earlier work [17]. The advantage of these approaches is that determining the XES spectra adds no significant computation cost relative to the cost of the Kohn-Sham DFT calculation, allowing large systems to be studied.

Carbon nanomaterials, including fullerenes and carbon nanotubes (CNT), have been the focus of considerable interest owing to their unique structural, mechanical and electronic properties. Spectroscopic methods are often used to characterise the structure of these materials. For example, Raman spectroscopy can provide information on the structure, bonding and environment of CNTs [18] and graphene [19], including details on CNT diameter, chirality and defects. One key mode is the radial breathing mode and the frequency of this mode is known to depend on the diameter of the CNT. A further band is the disorder-induced D band, which is associated with sp^3 defects in CNTs [20]. CNTs can also be studied using fluorescence [21] and nuclear magnetic resonance spectroscopies [22,23], and there has been a considerable effort focused on accurate simulations of the spectroscopy of these systems, for examples see references [24–30]. Spectroscopic studies have also shown that hydrogenation of fullerenes has a significant effect on its electronic structure. The ability to tune the photophysical properties of $C_{60}H_x$ has potential applications in a range of devices where carbon based materials have a number of advantages compared to commonly used transition metal based quantum dot chromophores [31].

Carbon nanomaterials have also been studied with X-ray spectroscopy. Kawai and Motoyama reported X-ray emission spectra for solid C_{60} and C_{70} [32]. The experimental spectra were compared with spectra simulated from the 2p density of states from a Hartree-Fock theory calculation. The X-ray emission spectrum of C_{60} has also been measured and calculated by Heggie and co-workers [33]. The core-hole was treated as a nitrogen impurity in the $Z + 1$ approximation and the spectrum simulated from the p-projected density of occupied states. The calculations reproduced the bands observed in experiment. Other fullerenes have also been studied, for example the X-ray emission spectra of different isomers of C_{82} have been calculated [34] and the X-ray emission spectrum of bulk K_3C_{60} measured [35]. The XES of hydrofullerene ($C_{60}H_{36}$) [36] and fullerene fluoride ($C_{60}F_{24}$) [37] has been studied. For both of these molecules, the distinct bands present in the X-ray emission spectrum of C_{60} are not evident and only a broad peak is observed. RIXS spectra have been reported for C_{60} and C_{70} [38,39]. For C_{60} there is a significant variation between the spectra excited at different photon energies.

X-ray emission spectra for nanotubes have also been reported [40–42]. In one study [40] four peaks were identified and spectra simulated based upon semi-empirical PM3 calculations using finite nanotube structures with the end carbons capped with hydrogen atoms. Only small differences between the spectra for zigzag and armchair nanotubes were observed. X-ray emission spectra of multi-walled nanotubes showed a small contraction in the high energy region of the spectrum with decreasing diameter [41]. Resonant X-ray emission spectra showed a strong dependence on the diameter of the tubes at an excitation energy of 285.5 eV, corresponding to a core$\rightarrow \pi^*$ excitation [43]. It was suggested that this might provide a technique to determine the mean tube diameter. In this paper DFT calculations are used to study the X-ray emission spectra of carbon fullerenes and nanotubes and study the sensitivity of the spectra to modifications of the structure. Subsequently, the extension of the calculations to study the RIXS spectra of these materials is explored.

2. Computational details

The structure of the fullerenes and nanotubes were optimised at the B3LYP/6-31G* level of theory [44,45]. The nanotube calculations used finite length nanotubes with enclosed (capped) ends,

similar to those used in previous work [25]. X-ray emission spectra were computed according to Eqs. (1) and (2) from a Kohn-Sham DFT calculation using the short-range corrected SRC1r1 exchange-correlation functional [10]. Details of the methodology underlying the calculations have been described fully elsewhere [16], and a more brief account is given here. In the SRC1r1 functional, the electron repulsion operator is partitioned according to

$$\frac{1}{r_{12}} \equiv C_{SHF} \frac{\text{erfc}(\mu_{SR} r_{12})}{r_{12}} - C_{SHF} \frac{\text{erfc}(\mu_{SR} r_{12})}{r_{12}} + C_{LHF} \frac{\text{erf}(\mu_{LR} r_{12})}{r_{12}} - C_{LHF} \frac{\text{erf}(\mu_{LR} r_{12})}{r_{12}} + \frac{1}{r_{12}} \quad (3)$$

The first and third terms of Eq. (3) are treated with HF exchange and DFT exchange is used for the remaining terms. The four parameters in the functional, C_{SHF}, C_{LHF}, μ_{SR} and μ_{LR}, determine the amount of Hartree-Fock exchange in the short and long range, and these parameters were optimised to reproduce a set of core-excitation energies [10]. Two sets of parameters were optimised, the first for excitations at the K-edge of first row nuclei and the second for excitations from second row nuclei, and these functionals are denoted SRC1r1 and SRC1r2, respectively. These functionals correct the orbital energy of the core orbitals and result in more accurate transitions energies for X-ray emission when evaluated from the different in the orbital energies. In the evaluation of the transition matrix elements to determine the intensity, the final and initial states are approximated by the valence and core molecular orbitals associated with the transition (see Eq. (2)).

The 6-31G* basis set was also used for the calculations of the X-ray emission spectra. For C_{60}, there is little difference between the spectrum computed with this basis set and spectrum computed using the larger 6-311G* basis set except that the spectrum for the 6-31G* is about 0.4 eV higher in energy. A comparison between these two calculated spectra is shown in Supplementary Content. However, the small size of this basis set allows larger systems to be studied more readily. Spectra were generated by convoluting the transitions with Lorentzian functions with a width of 1 eV. All calculations were performed with the Q-CHEM software package [46].

A RIXS spectrum for C_{60} was computed using a similar approach but with a reference determinant corresponding to a core to lowest unoccupied molecular orbital (LUMO) excited state. C_{60} has three degenerate LUMOs, however, the resulting spectrum does not depend on which of these are occupied. The core excited state is maintained during the self-consistent field calculation by using the maximum overlap method [47]. The B3LYP functional in conjunction with the 6-31G* basis set was used for these calculations as suggested by previous work [16]. A spectrum is also computed by averaging over 100 structures taken from an *ab initio* molecular dynamics simulation for the excited state. These structures were sampled at equal time intervals from a 24 femtosecond simulation at 300 K.

3. Results and discussion

Fig. 1 shows the computed and experimental non-resonant X-ray emission spectra for C_{60} and C_{70}. For both C_{60} and C_{70} the calculations reproduce the shape of the experimental spectra well, although the calculations predict the transition energies to be too high, and the calculated spectra need to be shifted by −1.4 eV to align with experiment. The spectra have been decomposed into contributions from σ and π orbitals. The most intense bands in the spectra correspond to transitions from σ orbitals, while the high energy bands at 281.7 eV and 283.0 eV in C_{60}, and 280.8 eV and 282.7 eV in C_{70} arise from π orbitals. In general the two molecules have similar spectra. One noticeable difference is the relative